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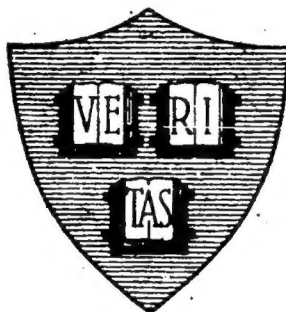
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FERROMAGNETIC RESONANCE ABSORPTION  
IN COBALT SINGLE CRYSTALS



By

Taiichiro Ohtsuka

August 30, 1953

Technical Report No. 187

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# Ferromagnetic Resonance Absorption in Cobalt Single Crystals

by

Taiichiro Ohtsuka

Cruft Laboratory, Harvard University

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## Abstract

Ferromagnetic resonance absorption of cobalt single crystals has been measured at  $\sim 24,200$  Mc/s. The temperature range was restricted to  $200^{\circ}\text{C}$  ( $180^{\circ}\text{C}$  to  $380^{\circ}\text{C}$ ) due to the high anisotropy energy and the phase transition at  $430^{\circ}\text{C}$ . The anisotropy constants  $K_1$  and  $K_2$ , the g-factor and the line width were determined at these temperatures using three single crystals of different crystallographical orientation.

## I

### Introduction

A considerable number of measurements on ferromagnetic resonance absorption have been made since the discovery of the phenomenon by Griffiths in 1940.<sup>1</sup> Most of the measurements, however, have been made on polycrystals and, in cases of single crystals, materials cubic in structure. Except for the data reported in Griffiths' first paper there seems to have been no measurements made on cobalt which as a single crystal possesses a hexagonal lattice. The primary difficulty which confronts one in performing resonance measurements on cobalt is its high anisotropy energy. Thus a field of the order of 10,000 oersteds is required to assure saturation in polycrystalline cobalt. For this reason one cannot rely too much on the data presented by Griffiths who found resonance at 510 oersteds for  $\lambda = 3\text{cm}$  in polycrystalline cobalt. Although the saturation problem can be avoided by using a single crystal in the easy direction, the use of single crystals does not eliminate the difficulty presented by the high anisotropy energy as we shall see later.

Ferromagnetic resonance absorption was first treated theoretically by Kittel.<sup>2</sup> He showed that the phenomenon can be described by solving a classical equation of motion having the form,

$$\frac{dM_{xy}}{dt} = \gamma [\vec{M} \times \vec{H}_{eff.}]_{x,y} - \frac{M_{x,y}}{T_2} \quad (1a)$$

$$\frac{dM_z}{dt} = \gamma [\vec{M} \times \vec{H}_{eff.}]_z - (M_z - M_0)/T_1 \quad (1b)$$

Here  $\gamma = ge/2mc$  and  $g$  is the so-called spectroscopic splitting factor. The dampening terms are the same as those adopted by Bloembergen<sup>3</sup> based on the form introduced by Bloch for nuclear magnetic resonance. The essential point in Kittel's discussion was to note that one had to take into consideration the field due to shape demagnetization and anisotropy besides the external field in the quantity  $\vec{H}_{eff}$ . In general one can write  $\vec{H}_{eff}$  as,

$$\vec{H}_{eff} = \vec{H}_{ext} + \vec{H}_S + \vec{H}_a + \vec{H}_{exch} + \vec{H}_{st} \quad (2)$$

where  $\vec{H}_{ext}$  is the external field,  $\vec{H}_S$ , the demagnetizing field,  $\vec{H}_a$  the anisotropy field,  $\vec{H}_{st}$  the effective field arising from strain and  $\vec{H}_{exch}$  the effective field due to increase in exchange energy arising from an inhomogeneous distribution of magnetization. In our case  $\vec{H}_{st}$  can be neglected. The quantity  $\vec{H}_{ext}$  is proportional to  $\nabla^2 \vec{M}$  and hence zero if the sample is uniformly magnetized. It has been shown by Kittel and others to be negligible unless one goes down to very low temperatures where the skin depth becomes small. Although our sample was not of the shape that would ensure perfect homogeneity, the magnetization can be considered sufficiently homogeneous to render the quantity negligibly small as compared to the other terms when one considers the dimension ratios of the sample used and also the fact that only the middle portion of the sample facing the small aperture was subject to the r-f field. The equation of motion can now be solved by inserting

$$(\vec{H}_{ext})_x = h e^{i\omega t}, (\vec{H}_{ext})_y = 0, (\vec{H}_{ext})_z = H_0$$

and by putting  $M_{x,y} = m_{x,y} e^{i\omega t}$ . Here  $h$  is the amplitude of the r-f magnetic field which is applied perpendicular to the external field  $H_0$ . The steady-state solutions are

$$m_x = \frac{\gamma^2 M_z \left\{ H_0 + \sum (N_y - N_z) M_z \right\} h}{\left[ i\omega + \left( \frac{1}{T_2} \right) \right]^2 + \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_z \right\} \left\{ H_0 + \sum (N_y - N_z) M_z \right\}} \quad \dots (3a)$$

$$m_y = \frac{\gamma^2 M_z \left( i\omega + \frac{1}{T_2} \right) h}{\left[ i\omega + \left( \frac{1}{T_2} \right) \right]^2 + \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_z \right\} \left\{ H_0 + \sum (N_y - N_z) M_z \right\}} \quad \dots (3b)$$

and the resonance condition is given by

$$\omega_0^2 = \gamma^2 \left\{ H_0 + \sum (N_x - N_y) M_0 \right\} \left\{ H_0 + \sum (N_y - N_z) M_0 \right\} + \frac{1}{T_2^2} \quad \dots (4)$$

where we have put  $M_z = M_0$ , and

$$\sum (N_x - N_y) = (N_x^S - N_y^S) + (N_x^a - N_y^a) \quad \dots (5a)$$

$$\sum (N_y - N_z) = (N_y^S - N_z^S) + (N_y^a - N_z^a) \quad \dots (5b)$$

Here the effective fields due to shape demagnetization and anisotropy have been conveniently replaced by effective demagnetization factors,  $N_x^S, N_y^S, N_z^S$  and  $N_x^a, N_y^a, N_z^a$ , respectively. A general formula for deriving the effective fields and the effective demagnetization factors from the knowledge of the expression of energy has been derived by MacDonald.<sup>4</sup> In the case of cobalt, which has an hexagonal structure and is magnetically uniaxial, the easy direction of magnetization lying along the hexagonal axis, the anisotropy energy can be expressed phenomenologically from symmetry considerations as follows,

$$E_a = K_1' \sin^2 \theta + K_2' \sin^4 \theta + \dots, \quad (6)$$

where  $\theta$  denotes the angle between the hexagonal axis and the direction of magnetization. As for fitting the magnetization curve, it has been shown that higher-order terms are not necessary. It is also known that in cobalt the hexagonal plane is isotropic within experimental errors. From Eq. (6) MacDonald obtains the following expression for the effective demagnetizing factors of anisotropy,

$$(N_x^a - N_z^a) = \frac{2}{M_0} [(K_1' + 2K_2')(\gamma_{zx'}^2 - \gamma_{xx'}^2) + 2K_2'(3\gamma_{xx'}\gamma_{zx'} - \gamma_{zx'}^2) \gamma_{zx'}^2] \dots (7a)$$

$$(N_y^a - N_z^a) = \frac{2}{M_0} [K_1' + 2K_2'(\gamma_{zx'}^2 - \gamma_{yx'}^2) + 2K_2'(3\gamma_{yx'}\gamma_{zx'} - \gamma_{zx'}^2) \gamma_{zx'}^2] \dots (7b)$$

Here the primed coordinates refer to the coordinate system of the principal axes of the crystal and the unprimed ones to the coordinate system of the applied field.  $\gamma_{ij}$  is the direction cosine connecting the two coordinate systems. In the actual calculation, the expression for the anisotropy field is first derived in the coordinate system of the crystal. Secondly, the effective demagnetization factors are derived and then transformed to the system of the external field which is the actual laboratory coordinate system. Thus  $N_x^a, \dots$  are actually tensor quantities and should read  $N_{xx}^a$ , etc. The off-diagonal terms are not precisely zero but are known to be very small. To obtain a linear relation between the effective field and magnetization, i.e.,  $H_{\text{eff}}^a = \sum N^a M_0$ , the quadratic terms of  $m_{x,y}$  have been neglected. This is reasonable because  $m_{x,y} \ll M_0$ . From Eqs. (3a), (3b) and the relation for high-frequency susceptibility,

$$\mu - 1 = \mu_1 - 1 - i\mu_2 = 4\pi\chi = \frac{4\pi m_x}{h} \quad (8)$$

one obtains for the real and imaginary parts of the permeability the following expressions,

$$\mu_1 = \frac{4\pi\gamma^2 M_0 \{ H_0 + \sum (N_y - N_z) M_0 \} (\omega_0^2 - \omega^2)}{(-\omega^2 + \omega_0^2)^2 + \frac{4\omega^2}{T_2}} \quad (9a)$$

$$\mu_2 = \frac{4\pi\gamma^2 M_0 \{ H_0 + \sum (N_y - N_z) M_0 \} \frac{2\omega}{T_2}}{(-\omega^2 + \omega_0^2)^2 + \frac{4\omega^2}{T_2}} \quad (9b)$$

Thus by measuring the frequency, the field for resonance, and the permeability, one can obtain values for the g-factor and the anisotropy constants from (4), (5a, b) and (7a, b) and the quantity  $T_2$  from Eq. (9a) and (9b). In

the experiment to be described these quantities were derived for cobalt single crystal at a frequency of about 24,200 Mc/s (K-band).

## II

### Samples

Three cobalt single crystals cut in different orientations were kindly lent us through the courtesy of Professor Y. Shirakawa of the Tohoku University, Japan. All three were in the shape of thin rectangular slabs. The important dimensions are listed in Table I. Here  $\theta$  denotes the angle between

Table I*				
Specimen	Width	Thickness	$\theta$	Length of Span
[0001] axis	0.107"	0.0209"	11.2°	0.539"
[2112]	0.115"	0.0214"	53.8°	0.432"
[2110]	0.107"	0.0165"	80°	0.345"

the long axis of the rectangle and the hexagonal axis. In all our experiments the external field was applied along the long axis. Therefore  $\theta$  coincides with the angle between the direction of magnetization and the hexagonal axis.

In performing resonance measurements with ferromagnetic conductors, one has to be very careful in the preparation of the surface as the skin depth is very small ( $\sim 10^{-5}$  cm) at microwave frequencies. Thus very small surface strains will suffice to obscure the resonance completely. As has been shown by Kip and Arnold the resonance field will show practically no difference for different orientation of single crystals if the surface is merely mechanically polished. It is necessary to electropolish the sample in order to remove the minute scratches and surface strains. The electropolishing bath employed consisted of 90 per cent phosphoric acid and 10 per cent chromic acid. Good results were obtained when a current of 10 amp/cm<sup>2</sup>

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 For further details, see K. Honda and Y. Shirakawa, Sci. Rep. Tohoku University. A, 1, 9. (1949).



was fed with the sample as the anode and a copper plate for the cathode. It required about 3 to 4 minutes with the bath at room temperature in order to attain a smooth, shiny surface. The polishing process was continued until microscopic examination revealed no traces of scratches.

As already known, the only form that insures homogeneous magnetization is an ellipsoid. In our case the form was a rectangular slab. However, it was of such a dimension as to permit approximation as a prolate ellipsoid. The demagnetization factors were calculated by the formula derived by Osborn. The value for  $N_z^S$  was about 0.3. As the x- and y-components only see a thickness of one skin depth,  $N_x^a$  can be taken as zero whereas  $N_y^a$  can be taken as  $4\pi$ .

### III

#### Experimental Technique

The experimental technique was similar to the method employed by Bloembergen:<sup>3</sup> The sample was placed at the end of a rectangular microwave cavity which was excited by an r-f frequency field, and the power reflected was measured as a function of the external static field. The sample was placed in a position where the r-f electric field is zero and the r-f magnetic field is directed perpendicular to the static field. A block diagram of the apparatus is shown in Fig. 1. The power absorbed in the sample can be determined by measuring the unloaded  $Q$ ,  $Q_u$ , and the external  $Q$ ,  $Q_e$  of the cavity.  $Q_u$  is related to  $Q_e$  by  $Q_u = \beta Q_e$ .  $\beta$  is the so-called coupling parameter and for an undercoupled cavity is equal to  $1/R$ , where  $R$  is the voltage-standing-wave ratio (VSWR). Owing to the shape and dimensions of our sample, we were not able to adopt the conventional method of terminating the guide with the sample or placing the sample inside the cavity. As seen in Section II, the samples made available were in the form of thin rectangular slabs about 0.4 in. long, 0.1 in. wide and 0.02 in. thick (Table I). It was found necessary to align the magnetic field along the long axis of the crystal. Otherwise the demagnetizing factor would be either meaningless or prohibitively large because of the large saturation magnetization of cobalt ( $M \cong 1400$  gauss). Thus if one attempts to apply the field normal to the surface the demagnetizing field would amount to about  $4\pi M \cong 18,000$  gauss. This fact imposed



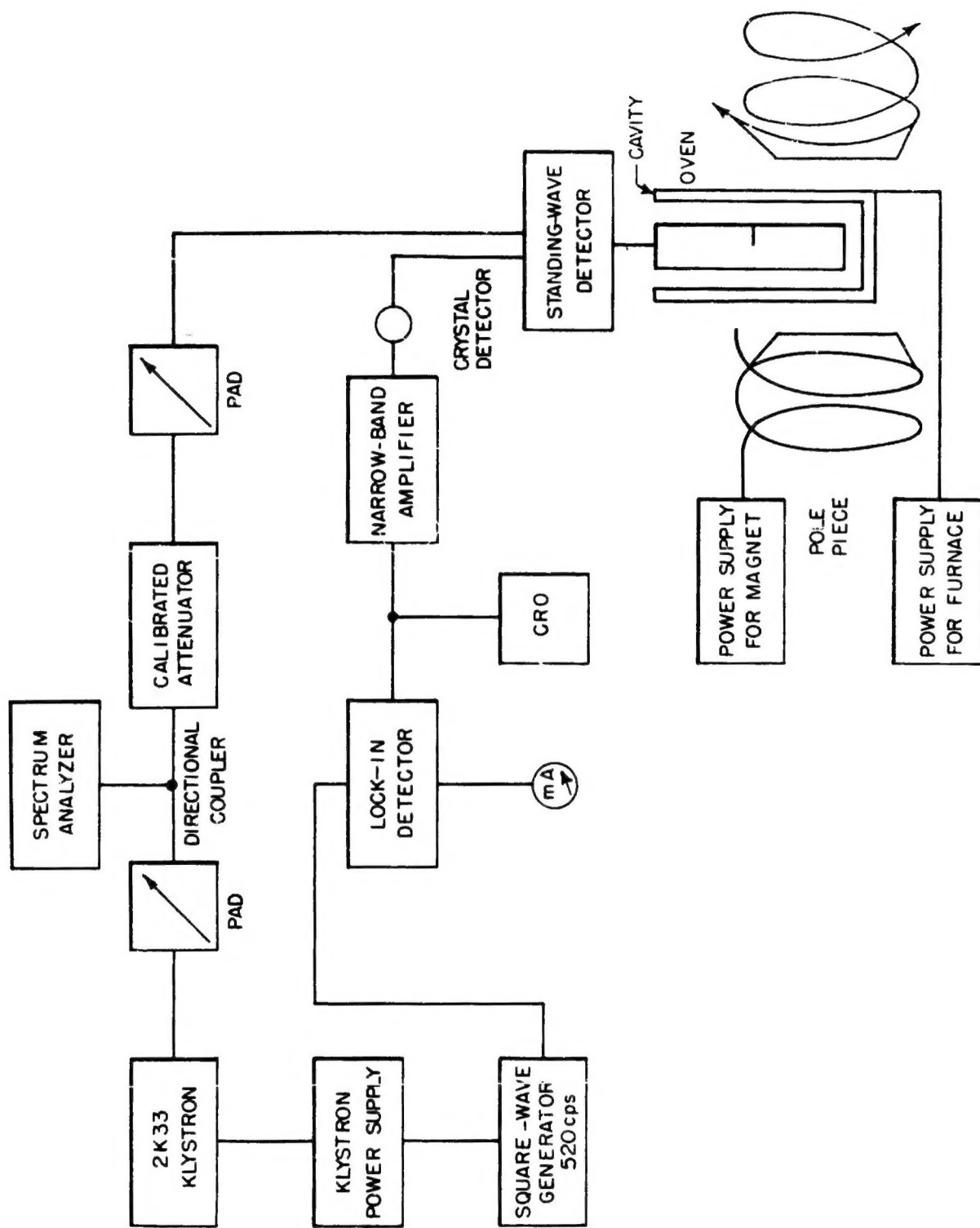


FIG. 1 BLOCK DIAGRAM OF APPARATUS

restrictions on the geometry of the sample relative to the cavity. Secondly, the crystal could not be silver-soldered on to the end wall of the cavity because of the existence of a phase transformation in cobalt at about  $430^{\circ}\text{C}$ . Soft soldering was rejected because measurements at temperature over  $300^{\circ}\text{C}$  were desired. Thus the cavity had to be constructed so that the crystal could be mechanically mounted with the long axis parallel to the external field.

Essentially three types of cavities were tested both at X-band and K-band. (a) A groove large enough to insert the crystal was cut in a copper block and the copper block as a whole was clamped on to the end of the guide. (b) A copper plate with a slit large enough to insert the crystal was silver-soldered on to the end of the guide. The sample was inserted in the slit and clamped on from the outside. (c) A copper plate with a small circular aperture in the middle was silver-soldered on to the end of the guide and the sample clamped on over the hole from the outside. Of the three, the first two, (a) and (b), were rejected for the following reasons. (a) At high temperatures (over  $150^{\circ}\text{C}$ ) the loss became prohibitively large. This is probably due to the fact that the contact between the end wall and the guide became bad and uneven due to thermal expansion. Furthermore, a haphazard behaviour in the reflected power as the magnetic field was applied was observed at higher temperatures. This is probably due to the fact that when the magnetic field is applied a mechanical torque works on the crystal if the field is not along the easy axis and if the sample is not perfectly aligned parallel to the field. The torque, although small, can be large enough to alter the electrical contact between the end wall and the guide, and hence affect the  $Q$  of the cavity. (b) Losses were too large. The  $Q$  in the X-band was already relatively low and in the K-band became too low to be measured. Cavity (c) was constructed with the object of eliminating all possible spurious effects resulting from changes in electrical contact of the end wall plus sample and guide, and also to cut down the losses to a minimum. As for the electrical contact, further precautions were taken by inserting a thin mica sheet between the end wall and the sample, which was clamped on from the outside so that the middle portion of the sample covered the aperture. Results were favorable, the unloaded  $Q$  being about 2500 at

room temperature and about 1800 at about 300°C. The only disadvantage of this type of cavity was that the available area of the sample was restricted, thus diminishing the change in reflected power due to resonance effects. The change in some cases was indeed small but, at the very smallest, well over the noise level of the lock-in detector output. Thus cavity (c) was adopted for all the measurements. Outside of the end wall, which shorted a section of the rectangular guide, the cavity was coupled through an asymmetrical iris and excited in the  $E_{102}$  mode. (The length of the cavity was therefore one guide-wave-length long (Fig. 2).)

The microwave power at about 24,200 Mc/s. was generated by 2K33 klystron. The power was square-wave-modulated at 520 cps and fed through paddings and a calibrated attenuator into the cavity. The reflected power was passed through a directional coupler and detected by a crystal detector. The detected signal was then passed through a 520 cps narrow-band amplifier and into the lock-in detector. The VSWR was measured by a slotted-line standing-wave detector. A portion of the microwave power was fed into a spectrum-analyzer in order to measure the frequency. The procedure of measurement was as follows; First, the unloaded Q was determined at zero field by measuring the VSWR as a function of frequency. Next, the external field was increased in appropriate steps and the VSWR measured at each field. Actually the VSWR was measured at one or two fields only. For the rest of the points only the reflected power was measured and R determined by the relation,

$$\frac{P_r}{P_i} = \frac{(1-R)^2}{(1+R)^2}$$

where  $P_r$  is the reflected power and  $P_i$  the incident power. This convenient procedure could be used because  $P_i$  is kept constant throughout the measurement. In all our measurements the cavity was undercoupled to the extent that  $P_r$  was about 15 to 20 per cent of  $P_i$ . This corresponds to a VSWR of about 2.

The static field was supplied by a conventional electromagnet. The field was determined by a flip coil which was calibrated at one point with a proton magnetic resonance. The gap between the pole pieces was about

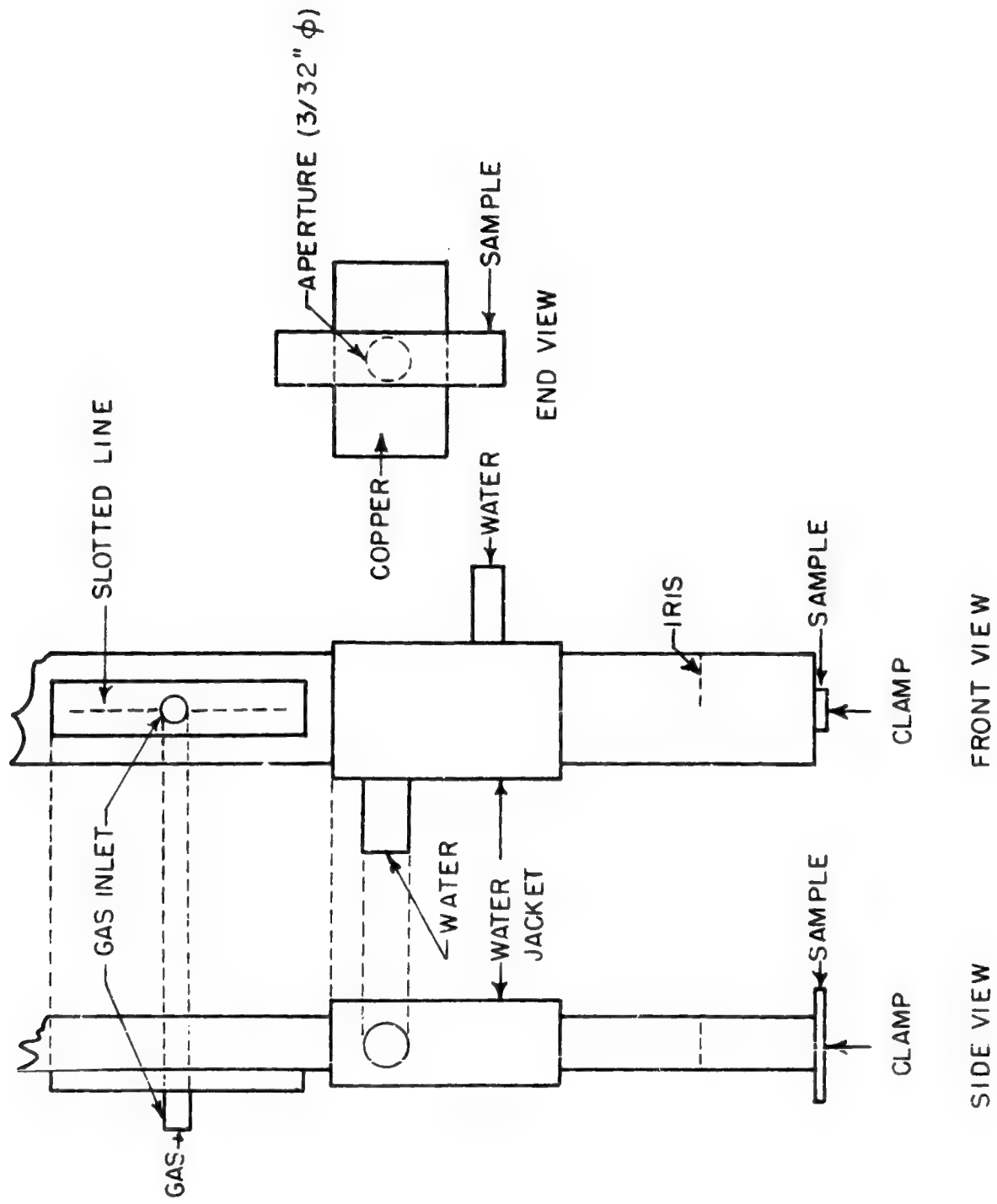


FIG. 2 DESCRIPTION OF CAVITY

3 inches. A field of about 7500 oersteds was attained with a current of about 10 amp. at 200 volts.

As we shall see later, it was found necessary to make all the measurements at elevated temperatures (200°C to 400°C). In order to prevent oxidation of the cavity and sample at these temperatures a gas consisting of 80 per cent nitrogen, 20 per cent hydrogen was introduced into the cavity. A mica sheet was inserted in one section of the guide to prevent the gas from escaping. A section of the guide was also water-cooled so that the heat would not extend to the whole apparatus. The outside of the cavity was merely flushed by the gas. This was sufficient to suppress the oxidation to an appreciable extent.

From the values of  $Q_u$  and  $R$  determined by the procedure described above, one can calculate the high-frequency permeability in the following manner: In our arrangement, only a small portion of the sample restricted by a circular aperture  $3/32$  in. in diameter is exposed to the microwave field. Thus we may assume that the introduction of the sample causes only a small perturbation. This is to say that the distortion of the field configuration in the cavity due to the introduction of the sample is negligibly small. Then one can employ the perturbation method developed by Bethe and Schwinger and others to derive the relation,

$$\frac{\delta f}{f} + j\delta\left(\frac{1}{2Q_u}\right) = \frac{\delta W}{W} \quad \dots (10)$$

Here  $f$  is the resonant frequency of the cavity and  $W$  the total stored energy of the cavity;  $\delta f$  and  $\delta W$  are the changes in these quantities due to the introduction of the sample. If the field configurations in the cavity are known,  $W$  and  $\delta W$  can be calculated in terms of  $\mu$ . Unfortunately it was difficult to determine the field configuration in the present set-up where the sample is clamped on from outside of the cavity. Accordingly one cannot hope to determine the absolute of  $\mu$  with exactness. However, the shape of the resonance curve ( $\mu$  versus  $H$ ) should be fairly good as  $\mu \sim \Delta Q$  and the relative values of  $\mu$  can be determined. It should be noted here that the  $\mu$  we are speaking of is the part of the complex permeability that determines the losses in the cavity. In a non-conducting material this is just the

imaginary part,  $\mu_2$ . In a ferromagnetic metal, however, the smallness of the skin depth at very high frequencies alters the situation and the losses are now determined by a so-called effective permeability

$$\mu_R = (\mu_1^2 + \mu_2^2)^{1/2} + \mu_2$$

Table II

Temp. °C	$K_1' \times 10^5 \text{ ergs/cm}^3$	$K_2' \times 10^5 \text{ ergs/cm}^3$	$(K_1 + K_2) \times 10^5 \text{ ergs/cm}^3$	g
180	4.57	10.8	15.3	2.65
200	2.92	9.16	12.1	2.50
220	.93	7.58	8.51	2.39
240	- 1.05	5.98	4.93	2.30
260	- 3.69	5.53	1.84	2.27
280	- 6.20	4.87	- 1.33	2.23
300	- 8.82	4.55	- 4.27	2.22
320	-11.3	4.49	- 6.77	2.22
340	-13.7	4.20	- 9.50	2.23
360	-15.7	4.11	- 11.6	2.24
380	-17.6	4.05	-13.6	2.28

## IV

Results

The anisotropy constant of hexagonal cobalt is known to be about  $6 \times 10^6 \text{ ergs/cm}^3$  at room temperature, an order of magnitude larger than that for iron and nickel. The effective field of anisotropy at room temperature turns out to be about  $\frac{2K_1}{M_0} \approx 7000 \text{ oe}$  and  $\frac{2K_2}{M_0} \approx 600 \text{ oe}$ , respectively.

Owing to this unusually high anisotropy field it requires a frequency of 30,000 Mc/s at zero applied field in order to observe resonance when the external field is applied parallel to the easy axis. Therefore in order to observe resonance at K-band (24,400 Mc/s) and at external fields high enough to warrant saturation it was necessary to go to higher temperatures where the anisotropy constants become sufficiently small. With the field applied along the easy axis, the resonance was first observed at about 150°C with an external field of about 1000 oersteds. For the difficult direction the resonance field at lower temperatures was much higher than the maximum field our magnet could produce. Thus the measurements at K-band were restricted to a relatively small temperature range of about 200°, the lower limit imposed by the high anisotropy field and the upper limit by the irreversible phase transformation which occurs at about 420°C. The range, however, covers the region where the switch in the axis of easy magnetization from the hexagonal axis to the hexagonal plane takes place.

The temperature dependence of the field of resonance  $H_0$  for the three crystals are plotted in Fig. 3. One can see qualitatively from this figure how the shift in the magnetic axis takes place. Bearing in mind the fact that the crystal nearest to the easy axis should resonate at the lowest field it is apparent that the shift does not take place abruptly, but gradually over a temperature range of about 100°, starting from about 220°C and ending at about 320°C, and that at about 270°C the 45° direction becomes the easy axis. The points of intersection in this figure cannot be taken too seriously due to the fact that the shape demagnetization factors for the three crystals are different. There is also about 1% difference in frequency. It is necessary to derive more significant quantities such as the anisotropy constants in order to look into the situation on a quantitative basis.

#### (a) Anisotropy constants

From the experimental values of  $H_0$  and frequency, and from the knowledge of the direction of the crystal relative to the principal axes, we obtain at each temperature three independent equations of the form Eq. (4). The unknown quantities are the  $g$ -factor and the two anisotropy constants  $K_1'$  and  $K_2'$ . Therefore the equations can be solved for  $K_1'$  and  $K_2'$  if we assume that the  $g$ -factor is isotropic. The assumption, although plausible, may be



open to question as the cobalt does not possess cubic symmetry. It is unfortunate that this point could not be checked directly as it would require a fourth independent equation if the  $g$ -factor is assumed anisotropic. Further discussions concerning this point will be made later. With the assumption of isotropic  $g$ -factor, the simultaneous equations which are quadratic in  $K'_1$ , and  $K'_2$  were solved by a convenient method of successive approximation. The results obtained for the anisotropy constants are shown in Table II and Fig. 4. The values for saturation magnetization were taken from recent measurements on cobalt single crystals made by Myers and Sucksmith.<sup>7</sup> It can be seen that  $K'_1$  is still rapidly changing whereas  $K'_2$  already shows tendency of levelling off. It is noted that we are still far below the Curie temperature which lies at about  $1000^\circ\text{C}$ . On the other hand we are quite near the temperature at which cobalt transforms from a hexagonal close-packed structure to a face-centered cubic structure (polycrystalline) which lies at about  $430^\circ\text{C}$ . Sucksmith and Myers have shown that for a single crystal the change in saturation magnetization takes place discontinuously at the transformation point. Presumably the anisotropy constants act similarly so it is not surprising that  $K'_1$  shows no indication of a minimum. The quantity  $K'_1 + K'_2$ , which is the difference in magnetic energy between the hexagonal axis and the hexagonal plane, has also been plotted. The dotted lines represent the results on  $K'_1 + K'_2$  calculated by McKeehan using the data on magnetization curves measured by Honda and Masumoto.<sup>8</sup> His results scatter somewhat on the scale used but one can see that it is roughly parallel to our results with a difference of about  $1 \times 10^5 \text{ erg/cm}^3$ . The anisotropy constants have also been calculated by Bozorth<sup>9</sup> using the same data. The general trend is again similar but the actual values are difficult to compare. Especially noticeable is the difference in the temperature at which  $K'_1$  changes sign. Bozorth's curve reads about  $200^\circ\text{C}$  whereas our curve reads  $228^\circ\text{C}$ . This temperature is particularly significant due to the fact that the magnetic axis starts to shift

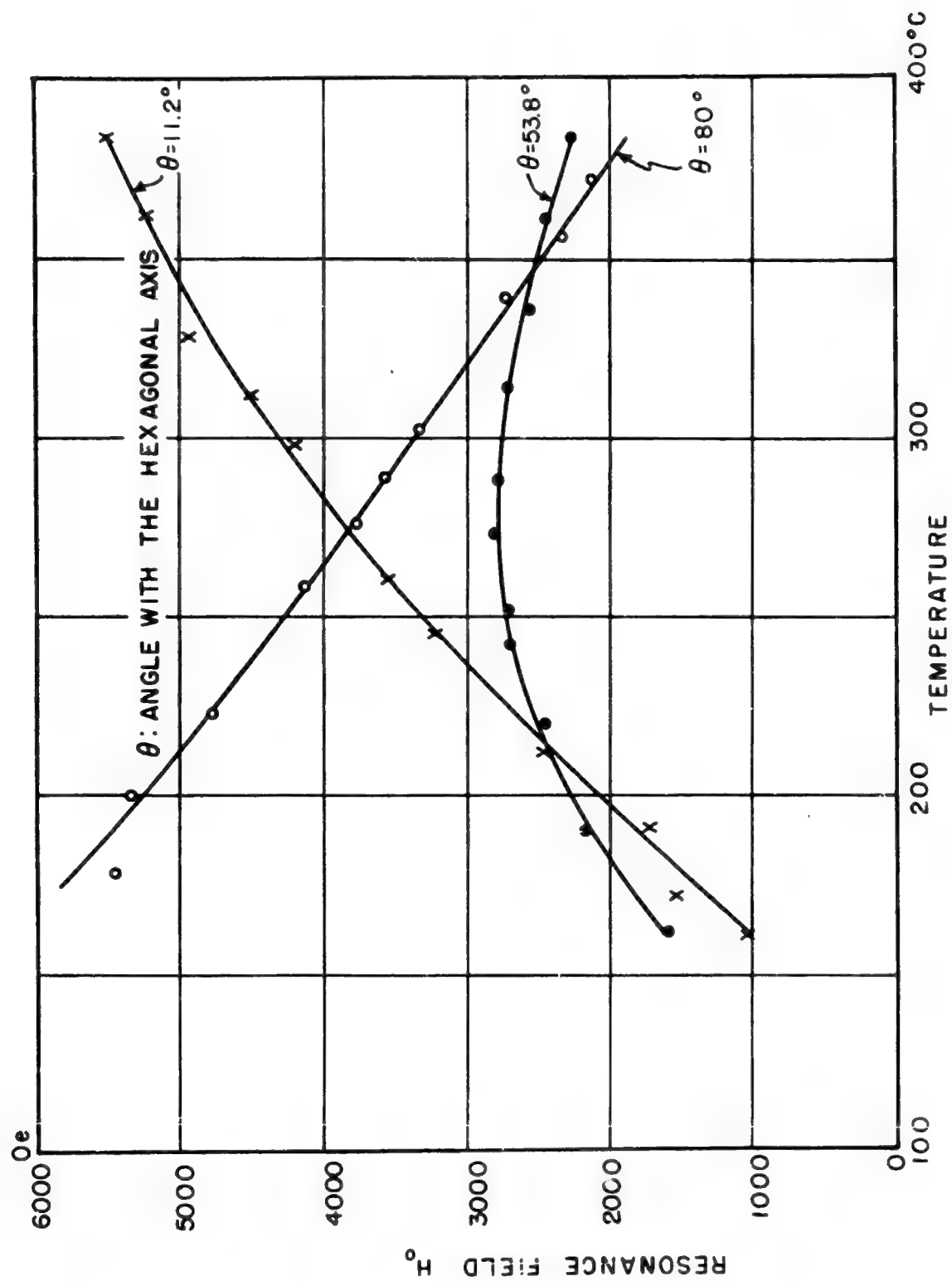


FIG. 3 RESONANCE FIELD  $H_0$  VERSUS TEMPERATURE  
IN COBALT SINGLE CRYSTALS

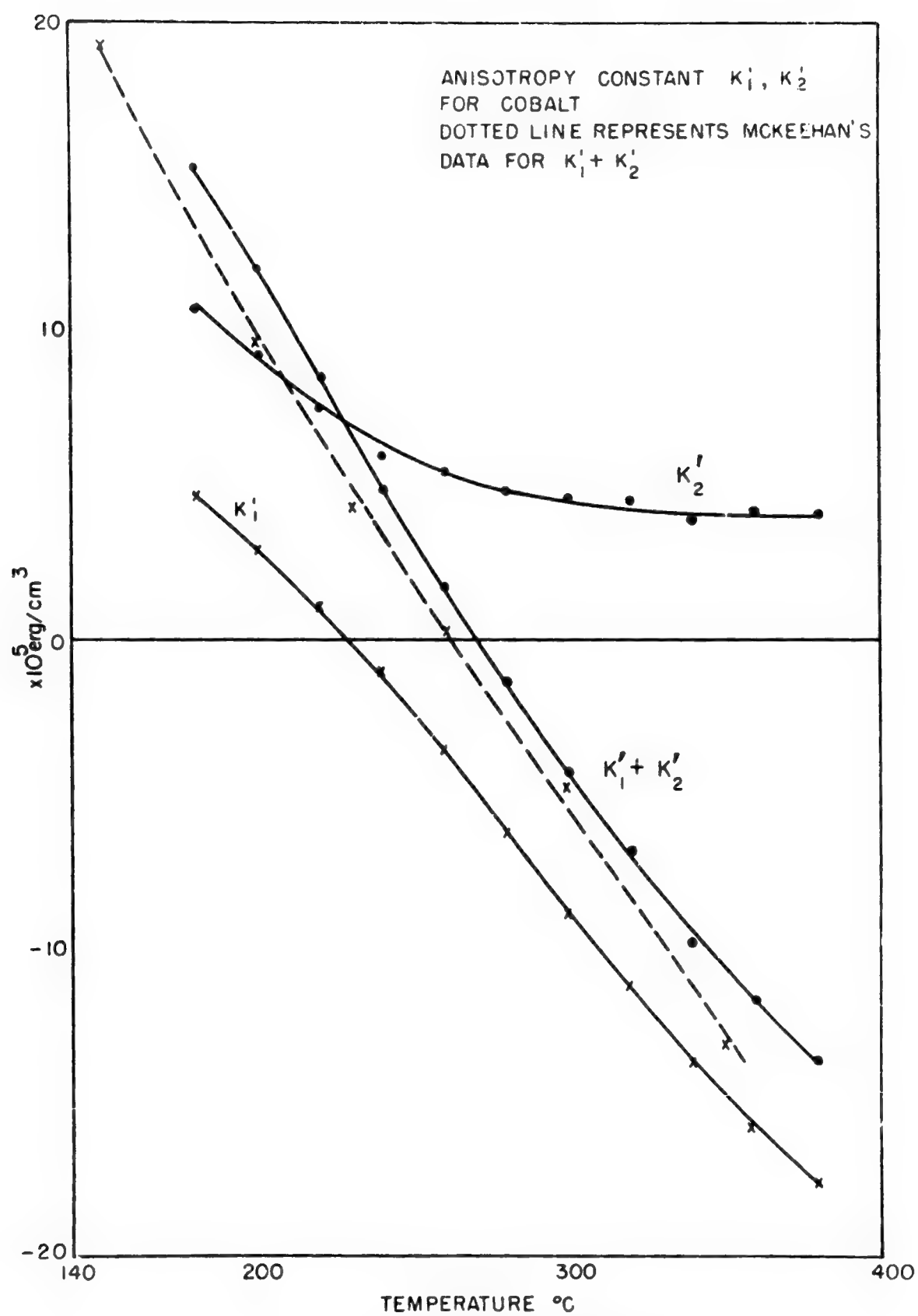


FIG.4 ANISOTROPY CONSTANTS  $K'_1, K'_2$

directions at this point. This can be seen in the following manner. The direction of easy magnetization is determined from the condition of minimum anisotropy energy; namely,

$$\frac{\partial E_a}{\partial \theta} = 0, \quad \frac{\partial^2 E_a}{\partial \theta^2} > 0$$

where  $E_a$  has the form as expressed in Eq. (6). Carrying out the differentiation, one finds,

$$\frac{\partial E_a}{\partial \theta} = K'_1 \sin \theta \cos \theta + 2K'_2 \sin^3 \theta \cos \theta = 0 \quad \dots (12a)$$

$$\frac{\partial^2 E_a}{\partial \theta^2} = K'_1 (\cos^2 \theta - \sin^2 \theta) + 2K'_2 (3 \sin^2 \theta \cos^2 \theta - \sin^4 \theta) > 0 \quad \dots (12b)$$

or

$$\theta = 0 \quad \text{when} \quad K'_1 > 0$$

$$\theta = \pi/2 \quad \text{when} \quad K'_1 + 2K'_2 < 0$$

In other words the easy direction will be parallel to the hexagonal axis as long as  $K'_1$  remains positive and in the hexagonal plane when  $-K'_1$  becomes larger than  $2K'_2$ . In between these values the easy direction will not lie along the principal axes and will be determined by the solution of Eq. (6) with  $\sin \theta \neq 0$  and  $\cos \theta \neq 0$ , i.e.,

$$\sin \theta = \sqrt{-\frac{K'_1}{2K'_2}} \quad (13)$$

The temperature range at which the magnetic axis takes intermediate directions can be determined from the known values of  $K'_1$  and  $K'_2$ . A plot of  $K'_1 + 2K'_2$  was made and it was found that  $K'_1 + 2K'_2 = 0$  corresponded to  $303^\circ\text{C}$ . Thus the magnetic axis starts to deviate from the hexagonal axis at  $228^\circ\text{C}$  and ends in the hexagonal plane at  $303^\circ\text{C}$ . The direction of easy magnetization in between these temperatures was calculated

from Eq. (7) and is shown in Fig. 5.

Although the origin of ferromagnetic anisotropy is generally believed to lie in the interplay between spin-orbit coupling and orbital valence, the theory itself is still far from satisfactory. Apart from computational difficulties, a basic defect is that the theories do not predict a correct temperature variation. Thus it is, unfortunately, not possible to compare our results in detail with theory. Vonsovsky,<sup>10</sup> however, has computed the temperature dependence of  $K'_1$  based on the Bloch-Gentile model<sup>11</sup> and has shown that under certain conditions it is possible for the sign to change. What he essentially shows is that at very high temperatures  $K'_1$  should be negative whereas at absolute zero it can be positive if certain restrictions are imposed on the relative magnitude of terms. The reason why these conditions may be allowed is not clear. Perhaps all one can say at the present is that the switch in the magnetic axis is determined by the temperature dependence of  $K'_1$ . It has been pointed out by Bloch and Gentile and Van Vleck<sup>12</sup> that the dipole-dipole coupling of pure magnetic origin yields much too small a value for  $K'_1$ . However, Van Vleck has shown that the spin-orbit coupling and the orbital valence produce an interaction which can be expressed as dipolar in nature. He called this a "pseudo-dipolar" coupling. In cubic crystals the first-order effect of pseudo-dipolar coupling is zero due to symmetry considerations. However, for hexagonal crystals the first-order effect does not drop out and this is what determines  $K'_1$ . In an ideally close-packed hexagonal crystal the nearest neighbors would not contribute to  $K'_1$ , but the further neighbor would. To sum up, it may be said that the shift in the easy direction from the hexagonal axis to the hexagonal plane arises from the temperature dependence of the first-order effect of dipolar coupling whereas the second-order effect tends to suppress the switch-over and spreads it out over a finite temperature range.

The accuracy of our results on  $K'_1$  and  $K'_2$  can be estimated as follows; As described previously,  $K'_1$  and  $K'_2$  are evaluated by assuming the g-factor to be isotropic and eliminating from Eq. (4) the variable  $\gamma$ . With three independent equations one then ends up with two independent equations which, after expanding the brackets, can be expressed as

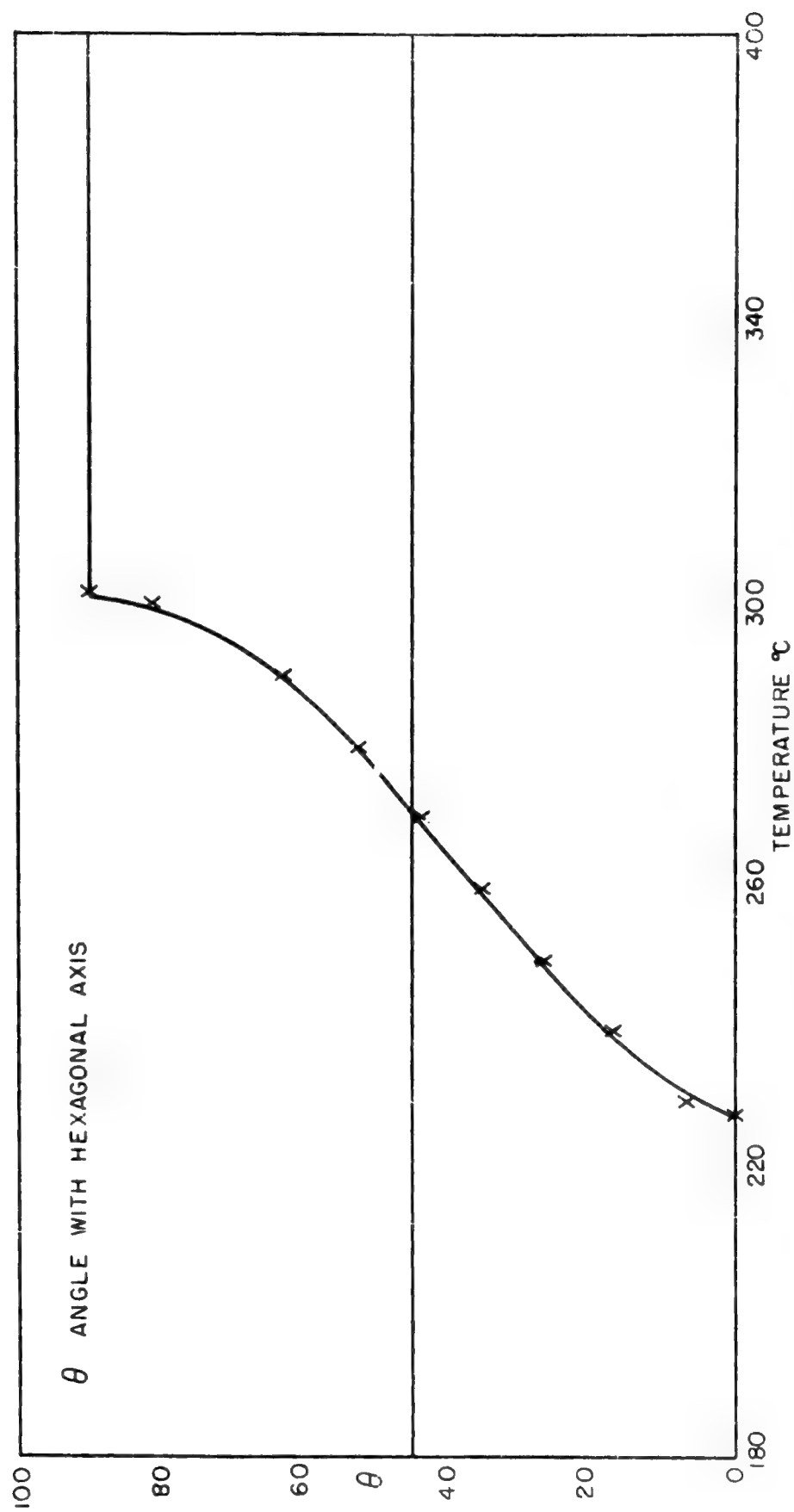


FIG. 5 DIRECTION OF AXIS OF EASY MAGNETIZATION VERSUS TEMPERATURE

$$u + x_1 K'_1 + x_2 K'_2 + (\text{terms quadratic in } K'_1, K'_2) = 0$$

$$u' + x'_1 K'_1 + x'_2 K'_2 + (\text{terms quadratic in } K'_1, K'_2) = 0$$

Actual computations show that a good approximation can be obtained with the quadratic terms neglected. The main errors arise from uncertainties in  $u, x_1, x_2$ , etc. In addition, there is also the so-called inherent error which is due to the interaction of errors in solving the simultaneous equations. Now the constants  $u, x_1, x_2$ , etc. involve the resonance field  $H_0$ , saturation magnetization  $M_0$ , shape demagnetization factor  $N$ , and the directional cosines of the angle between the hexagonal axis and the orientation of the crystal. Considering the fact that the results on  $M_0$  obtained by Myers and Suckamith were in good agreement with the results of Honda and Masumoto and that the values of  $M_0$  obtained by various authors on different crystals vary only by 0.3% at the most,  $M_0$  is probably good within 1 to 2% at the most. The error in  $H_0$  was not more than 3%.  $N$  is estimated to be good within 10%. The angle  $\theta$  is probably not more than  $2^\circ$  off. With these errors, one finds that the worst combination of errors results in an over-all error of about 6% in the anisotropy constants. The probable error will presumably be smaller.

#### (b) g-factor

The g-factor was obtained by inserting the evaluated anisotropy constants back into the resonance equation. The results show a steady decrease in the g-value from 2.6 at  $180^\circ\text{C}$  to 2.2 at about  $240^\circ\text{C}$ , at which point it tends to level off, and stay constant up to  $380^\circ\text{C}$  within experimental error (Fig. 6, Table II). This behavior is in contrast to previous experiments on ferromagnetic resonance which show that the g-value is practically independent of temperature. Thus it is rather striking to see a change in g with temperature amounting to about 20 per cent in a comparatively small temperature range and so far away from the Curie point. We shall first look into the sources of error which enter into the determination of g. By far the largest source comes from  $M_0$  and  $H_0$  which combine to give the leading term  $H_0 B_0$  in the resonance equation. Allowing a 1 per cent error for the frequency  $\nu$ , 2 per cent for  $M_0$ , and



3 per cent for  $H_0$  it turns out that  $\frac{\delta g}{g} = 2\%$ . The remaining terms contribute at the most 1 per cent. The g-factor is very insensitive to the shape demagnetizing factor and the anisotropy energy. For instance, a 30 per cent error in  $N$  or  $K'_1, K'_2$  will result in a error less than 0.5 per cent in  $g$ . Thus, altogether the g-factor should be good to about 3 per cent. On the other hand, the change in  $g$  amounts to about 20 per cent and it would require a 20 per cent error in  $H_0$  and  $B_0$  in order to account for the change as an error. It also is noted that the error must be a systematic one appearing at low temperatures if one wishes to make the  $g$  temperature-independent. Apart from the fact that an error of 20 per cent or more in  $H_0$  or  $B_0$  is highly improbable, it is difficult to see how a systematic error could enter. Furthermore, one notes that the saturation magnetization changes by only 3 per cent from  $180^\circ$  to  $400^\circ\text{C}$  and a change of more than 3 per cent in  $M_0$  at the low-temperature side would conflict with the temperature variation of  $M_0$ . Therefore, considerations of errors do not alter the essential feature of the anomaly. However, there are still reasons to believe that the anomaly may be spurious. This is due to the fact that in solving the simultaneous equations we conveniently assumed  $g$  to be isotropic. The g-factor, however, is in general a tensor quantity and there is no assurance that this assumption is correct. More explicitly, what we have assumed is that  $g_\perp = g_\parallel$  where  $g_\perp$  and  $g_\parallel$  are respectively the g-factors perpendicular and parallel to the hexagonal axis. Now the deviation  $\epsilon$  of  $g$  from the pure spin value of 2 is determined by the strength of the spin-orbit coupling and the splitting of the degenerate levels in the crystalline field of the solid, i. e.,  $\epsilon \sim \frac{\lambda}{\Delta}$  where  $\lambda$  is the spin-orbit coupling constant and  $\Delta$  the energy difference between the split levels. Although  $\lambda$  may be fairly isotropic, a slight deviation from cubic symmetry may cause considerable anisotropy in the level splitting  $\Delta$ . Whether this can explain the anomaly itself is still open to question because one still has to explain why the change takes place primarily on the lower temperature side. All this will have to be determined by future experiments at lower temperatures and in more than three orientations. It is probably premature to speculate any further until all the ambiguity is eliminated.

### (c) Line Width

As previously discussed (Sec. III), we were not able to determine the

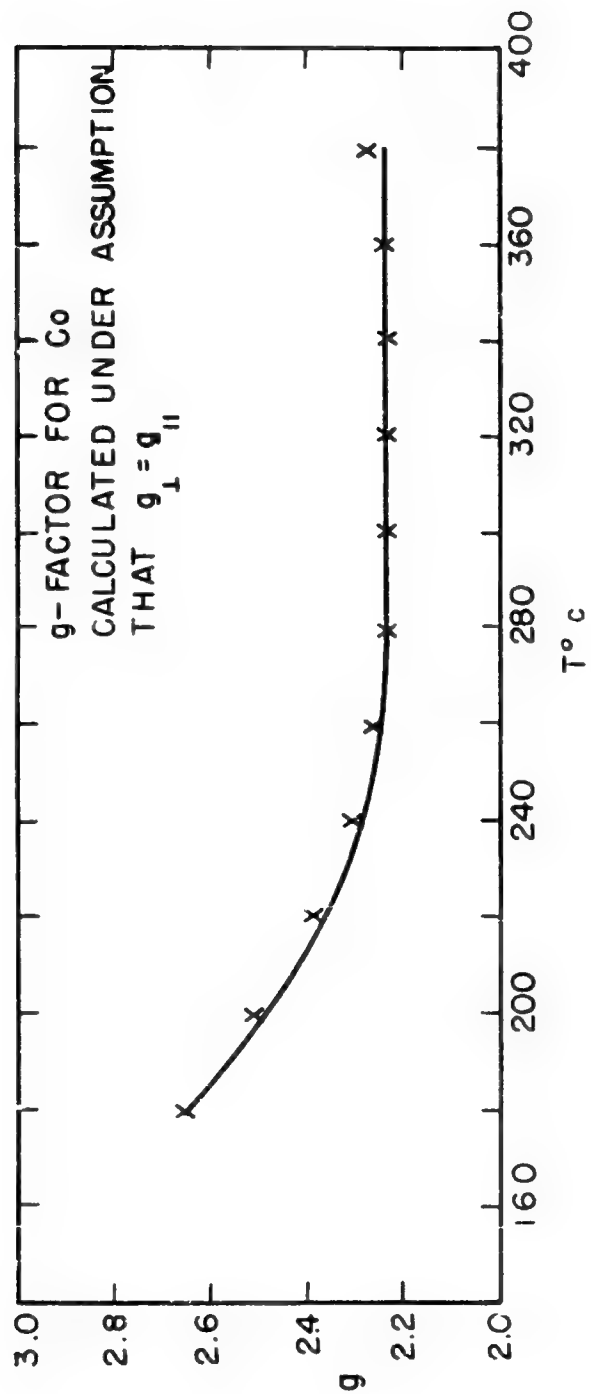


FIG. 6 g-FACTOR VERSUS TEMPERATURE

absolute value of  $\mu_R$ . However, relative values of  $\mu_R$  should suffice in the determination of the line width which depends on the shape of the resonance curve. Owing to the relatively small signal change arising primarily from the smallness of the effective sample value, the measurements on the line width cannot be relied on too much. Moreover, the fact that the sample was not of the form that would rigorously assure homogeneity in magnetization and that there did exist a small grain of different orientation in each crystal may well contribute to the line width although they are negligible as far as the shift in the central resonance frequency is concerned. Therefore detailed information, such as the difference in line width for different crystallographic orientations and the temperature dependency, was all within the limits of experimental error.

The line-widths for all three crystals were of the order of a few hundred oersteds. This corresponds to a relaxation time ( $T_2$ ) of the order of  $10^{-9}$  sec, a value normally yielded by ferromagnetic substances.

#### IV

#### Conclusion

The results obtained may be summarized as follows: Although the measurements had to be restricted to a relatively narrow temperature range, the interesting phenomenon of the reversal of sign in  $K_1$  already known from magnetization curve measurements has been definitely confirmed. Unfortunately the present state of theory does not allow detailed discussion of the phenomenon. The fact that resonance experiment is a more sensitive method of determining the anisotropy may permit one to confirm whether terms of higher order than  $\sin^4 \theta$  are really negligible or not. This would require another crystal of different orientation. It is highly desirable at this stage to perform the same experiments on a disk-shaped sample. This would enable one to get as many independent equations as necessary and therefore will not only determine whether or not higher-order terms in the anisotropy energy are necessary but also will eliminate ambiguity in the assumption of the isotropic g-factor. It is also desirable to extend the temperature range to much lower temperatures. This would require measurements at millimeter waves. A disk-shaped sample now becomes almost

mandatory, since at low temperatures one would have to work fairly close to the easy direction in order to insure saturation.

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